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**Low-Temperature Catalytic Oxidation
of Airborne Organic Materials**

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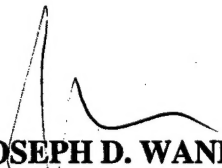
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ABSTRACT

Eltron Research Inc. has developed multi-component metal oxide catalysts for destruction of volatile organic compounds (VOCs) in air at low temperatures. The goal for this work is to produce a simple, cost-effective technology for reducing the concentration of VOCs in air to acceptable levels before the air is released into the atmosphere or recirculated. Specific applications include ventilated work spaces for spray painting and engine maintenance (degreasing and fuel line repair), indoor air decontamination, dry cleaning, food processing (grills and deep fryers), fume hoods, residential use, and solvent-intensive industrial processes. The components of the catalysts were chosen based on their anticipated oxygen surface mobility, moisture tolerance, multiple oxidation states, and documented activity for oxidation reactions. Catalyst powders and monolith-supported catalysts were screened for conversion of 1-butanol, toluene, and MEK to carbon dioxide and water. The concentrations of VOCs in the feedstream were maintained at ~100 ppm, and the space velocity was ~6,000 hr⁻¹. Catalysts highlighted in this document generated complete conversion of 1-butanol to CO₂ at 150°C, 69% conversion at 100°C, and 15% conversion at 80°C. For toluene, complete conversion was achieved at 200°C, and greater than 30% conversion at 150°C. Catalysts deposited onto cordierite monoliths retained their composition and activity, and were stable in humid air. However, sulfur- and phosphorous-containing compounds quickly poisoned these catalysts through formation of sulfates and phosphates.

INTRODUCTION

Increasing concern over detrimental environmental and health effects resulting from emission of volatile organic compounds (VOCs) has led to stricter emission regulation standards, and has fueled efforts to identify efficient and economical methods for VOC abatement. Conventional

noncatalytic methods for removing VOCs from gaseous waste streams include incineration¹ and carbon adsorption.² While both of these methods are effective, they require either special equipment and high temperatures, or secondary processing steps that are expensive to implement and maintain. Conversely, catalytic destruction of VOCs offers a less complicated and more economical and efficient emission control system than incineration or adsorption. Catalytic destruction occurs at much lower temperatures than incineration, and the reactors are simpler and cheaper to construct and operate. Furthermore, unlike adsorption methods, catalytic destruction is a one-step process for complete combustion of VOCs.

Traditionally, catalysts employed for destruction of VOCs are either metal oxides, or noble metals supported on relatively inactive materials such as Al_2O_3 or SiO_2 .³ While noble metal catalysts have higher activity for VOC destruction, metal oxides are cheaper and generally have greater resistance to poisoning from feedstream components. As with noble metal catalysts, metal oxides are active for combustion of VOCs with a range of organic functional groups.³⁻¹⁰ For example, the oxides of Fe, Mn, Mg, Ni, Co, V, Zn, Ti, Mo, Cr, and Cu have been used for the combustion of alcohols, aldehydes, alkanes, olefins, methane, and carbon monoxide at temperatures between 250°C and 450°C.³ Dispersion of noble metals such as Pt or Pd onto metal oxides can reduce the catalytic combustion temperature to a range between 100°C and 200°C, depending on the specific catalyst system and VOC. However, even with noble metal catalysts, the temperatures required to attain high activity generally are well above 100°C. A significant reduction in operating cost for catalytic VOC removal systems could be achieved by lowering the temperature range for activity of metal oxide catalysts, and avoiding the use of expensive precious metals.

The catalytic properties of CeO_2 -based materials have been thoroughly studied, and improvements in metal oxide oxidation catalysts have resulted from strategically modifying CeO_2 with other metal oxides.¹¹⁻¹⁵ CeO_2 without any additives or supported metals is active for oxidation of CO with light-off temperatures (50% conversion) above 300°C.¹⁴ However, by adding La to promote oxygen vacancies, and a small quantity of Cu (1 at. %), as either bulk CuO or incorporated into the structure, the light-off temperatures for CO oxidation were reduced below 100°C.¹⁴ Strong interactions between transition metal additives and metal oxides are largely responsible for the enhancement in catalytic activity. It is perceivable that active sites are formed by highly dispersed clusters of transition metal atoms and ions, which promote oxidation at the phase boundary between the cluster and metal oxide.¹⁴ It is anticipated that similar catalyst development strategies will be beneficial for VOC oxidation catalysts as well.

The objective of the work described in this manuscript was to develop multi-component metal-oxide catalysts with high activity for complete destruction of common VOCs at temperatures of ~200°C and lower. The performances of several proprietary catalysts for complete destruction of 1-butanol, toluene, and methyl ethyl ketone (MEK) will be presented. Catalysts were tested as powders and deposited onto ceramic support structures. It is anticipated that these catalysts and derivatives will be used to produce a simple, cost-effective technology for reducing the concentration of VOCs in air to acceptable levels before the air is released into the atmosphere or recirculated. Specific application areas include ventilated work spaces for spray painting and engine maintenance (degreasing and fuel line repair), indoor air decontamination, dry cleaning, food processing (grills and deep fryers), fume hoods, effluents from air stripping towers, wet-air oxidation, and solvent-intensive industrial processes.

EXPERIMENTAL

A. Catalyst Preparation

Powder catalysts were prepared by coprecipitation from appropriate mixtures of metal nitrates using $1M\text{NH}_4\text{OH}$. The precipitates were filtered and washed several times with cold water, then dried overnight at 120°C in air. The dried powders were ground, passed through a $150\text{-}\mu\text{m}$ sieve, then calcined in air at temperatures between 400°C and 500°C for several hours.

Supported catalysts were prepared on commercial cordierite monoliths (Corning) with 400 cells/in². Test monoliths had a diameter of 14 mm and height of 25 mm. Monolith samples were washed several times in methanol and dried at 200°C for 5 minutes prior coating with catalyst. A layer of Al_2O_3 was applied to the bare monoliths to increase surface area. This step was accomplished by repeatedly dipping the monolith into a boehmite solution followed by drying at 120°C for 2 hours. After three applications, the coated monolith was calcined for 2 hours at 400°C . This procedure increased the surface area from $2.4 \pm 0.3\text{ m}^2/\text{g}$ for the bare monolith to greater than $20\text{ m}^2/\text{g}$ with the Al_2O_3 coating. Catalysts were applied to the Al_2O_3 -coated monoliths by repeated dipping in an aqueous nitrate precursor solution followed by drying. The weight of catalyst precursors reached a maximum after four applications. After deposition of the nitrate precursors, the monolith samples were calcined in air at 400° to 500°C for 5 hours to produce the corresponding oxides.

B. Catalyst Screening

Figure 1 shows a simplified schematic diagram of the plug-flow apparatus used for catalyst screening. The apparatus incorporated four reactors, each consisting of a furnace surrounding a 4-mm i.d. (powder samples) or 14-mm i.d. (monolith samples) quartz tube containing the catalyst sample. Catalyst samples were held in place by pads of quartz wool and a section of a narrow inner tube. VOCs were introduced into the system from cylinders of 200 ppmv VOC/air mixtures (AirGas). The concentrations typically were adjusted to 100 ppmv by mixing the VOC supply with an air supply line. Flow rates and mixing ratios were controlled by needle valves and monitored using both ball-type and bubble flow meters. Reactor temperatures were measured and adjusted using controllers paired with thermocouples inserted in the quartz reactor tubes to a height touching the top of the catalyst bed.

The space velocity (SV) was calculated according to,

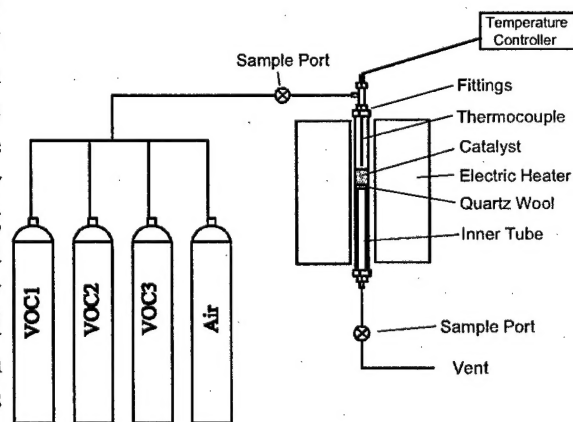


Figure 1. Schematic Diagram of the apparatus used for Catalyst screening.

$$SV = \frac{F_T}{V_c} = \frac{F_T}{\left(\frac{d}{2}\right)^2 ph} \quad (1)$$

where F_T was the total gas volume flow rate, V_c was the catalyst geometric volume, d was the inner diameter of the quartz sample tube, and h was the height of the catalyst bed in the sample tube. Approximately 0.2 g of catalyst was used for each evaluation, which resulted in a ~1-cm deep catalyst bed. Based on the catalyst geometric volume, VOC flow rates were adjusted to between ~3 and 70 mL/min to achieve space velocities between ~1,000 and 26,000 hr⁻¹. For monolith-supported catalyst, the data are more conveniently expressed in terms of the catalyst weight to flow rate, W/F , in units of g•s/cm³. Thus, for 0.2 g of catalyst on a monolith, and a flow rate of 12 mL/min, the $W/F = 1.0$ g•s/cm³.

Representative VOCs used in this work were toluene, 1-butanol, and MEK. These VOCs were chosen based on their use in spray paints and general popularity as solvents. Additionally, these VOCs represent different organic functionality, i.e., aromatic, alcohol, and ketone. Measurements of the inlet VOC concentration and outlet VOC and CO₂ concentrations were accomplished by sampling through ports located on opposite sides of the reactors. Prior to screening, catalyst samples were heated in line at 200°C overnight under flowing air. Inlet and outlet VOC concentrations were determined from chromatographic peak areas using a Shimadzu GC-14A with flame-ionization detection and a 1% AT 1000 Graphpac 60/80 column (Alltech). Product CO₂ concentrations were determined using a Hewlett-Packard 5890 GC with thermal-conductivity detection and a CTR-1 column (Alltech).

Percent conversion values (%C) were calculated according to,

$$\%C = \left(\frac{[CO_2]_{out}}{S[VOC]_{in}} \right) 100 \quad (2)$$

where $[CO_2]_{out}$ is the outlet CO₂ concentration, S is a stoichiometric factor (4 for 1-butanol and 7 for toluene), and $[VOC]_{in}$ is the VOC inlet concentration. Reaction rates also were calculated based on outlet CO₂ according to,

$$Rate = \frac{F_m X_{CO_2}}{SW_{cat}} \quad (3)$$

where F_m is the total molar gas flow rate, X_{CO_2} is the outlet mole fraction of CO₂, and W_{cat} is the catalyst sample weight. Using this equation with the stoichiometric factor S expressed the reaction rate as moles of VOC destroyed per second per gram of catalyst.

RESULTS AND DISCUSSION

A. Mixed-Metal-Oxide Catalysts

Figure 2 contains a summary of catalytic activity for conversion of 1-butanol to CO_2 for three powdered multi-component metal oxide catalysts, MMO1 through MMO3, at 80°C (dotted), 100°C (black), and 150°C (gray). These catalysts contained no precious metals. The concentration of 1-butanol was 100 ppmv in air, and the space velocity was 6,000 hr^{-1} . For comparison, screening results for the single-component parent metal oxides MO1 and MO2, and a commercial 1%Pt/ Al_2O_3 catalyst (Alfa Aesar, surface area 300 m^2/g) were included as well. The conversion and rate values shown in Figure 2 were averages of steady-state measurements taken after approximately 10 to 24 hours at each temperature. Comparing the data at 150°C,

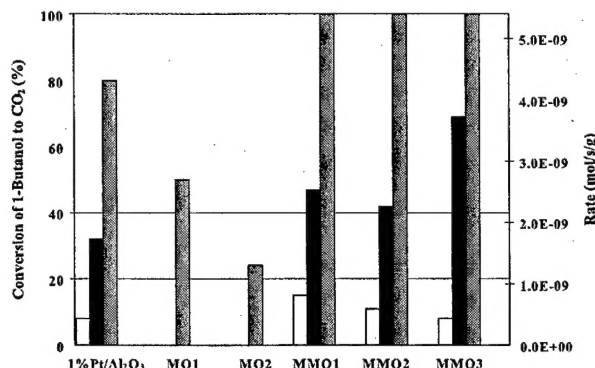


Figure 2. Plot showing the conversion of 1-butanol to CO_2 at 80°C (dotted), 100°C (black), and 150°C (gray) for several catalyst compositions (powder). The 1-butanol concentration was 100 ppm in air, and the space velocity was $\sim 6,000 \text{ hr}^{-1}$. MO1 and MO2 correspond to single-component metal oxides, and MMO1, MMO2, and MMO3 were multi-component oxides derived from MO1 and MO2. The 1%Pt/ Al_2O_3 was obtained commercially (Alfa Aesar) and was included for comparison.

the MMO catalysts all generated 100% conversion, whereas the unmodified metal oxides generated only 50% and 24% conversion. The most active catalyst was MMO3, which improved the low-temperature activity by more than 50°C relative to MO1. Moreover, all of the MMO catalysts performed better than commercial 1%Pt/ Al_2O_3 , which was significant since none of the Eltron catalysts in Figure 2 contained expensive precious metals. Since the MMO catalysts primarily were combinations of MO1 and MO2, these results indicated that significant improvements in catalyst activity could be achieved through relatively minor modifications in catalyst composition. Furthermore, the dramatic increase in activity achieved by compositing metal oxides underscores the beneficial synergy between these materials for low-temperature combustion.

The catalyst compositions designated as MMO1 and MMO3 in Figure 2 were subsequently tested deposited onto cordierite monoliths. Attempts to deposit slurries of catalyst powder onto support structures resulted in pore clogging and nonuniform layers with very poor catalyst adhesion. Alternatively, deposition by decomposition of nitrate precursors, as described above, gave very uniform and structurally stable films. Moreover, since this method was not subject to problems associated with selective precipitation, the target catalyst compositions were achieved easily. Figure 3 shows magnified images (26x) of monolith sections before and after catalyst deposition. The section without catalyst contained 13 wt.% alumina, which was barely visible at this magnification. The lack of an obvious alumina film suggested that the sol-gel deposition procedure produced an even and relatively dense coating. The image on the right shows a very thick (26 wt.%) catalyst layer with large catalyst grains and high porosity. Even at this level of catalyst loading and higher, the coating remained adhered to the walls, and the cells were unobstructed through the length of the monolith section.

Figure 4 summarizes the effect of catalyst loading (MMO1) on BET surface area, percent conversion of toluene to CO_2 , and the rate of toluene destruction. Rather than space velocity, W/F was used instead since the nature of the sample was so much different from powders. Specifically, the plug-flow reactor volume with powder samples was only 0.13 cm^3 , which corresponded to a space velocity of $6,000 \text{ hr}^{-1}$ and a residence time of $\sim 0.6 \text{ sec}$ at a flow of 12 mL/min . However, for monolith testing the *same* mass of catalyst was distributed over a much larger volume

of 2.3 cm^3 , which corresponded to a space velocity of only 300 hr^{-1} and a residence time of almost 10 sec . Since approximately 2 cm^3 of this total volume was empty space, space velocity calculations dramatically underestimated the activity of monolith samples, and W/F was deemed more appropriate. Figure 4 demonstrates that as catalyst loading increased from 12% to 32%, there was a corresponding increase in BET surface area from 21.8 ± 0.1 to $69 \pm 3 \text{ m}^2/\text{g}$. This surface area approached the value for the unsupported powder of $81.9 \pm 0.7 \text{ m}^2/\text{g}$. Despite these differences in loading and surface area, the percent conversion of toluene to CO_2 increased only slightly, as shown in the inset of Figure 4. Furthermore, as also shown in the inset, the rate of toluene destruction per gram of catalyst decreased significantly as loading increased. The highest percent conversion at 200°C was 92%.

Monolith-supported MMO2 demonstrated higher activity for toluene destruction than MMO1, with a maximum at 17 wt.% catalyst-loaded. This sample generated 100% conversion at 200°C , and 29% at 150°C . As with MMO1, these conversion values agreed almost perfectly with the values for the powder given in Figure 2. Highest activity was achieved for monolith-supported MMO3. Both a 6 wt.% and 26 wt.% catalyst-loaded sample demonstrated 100% destruction of toluene at 200°C . This result was particularly significant for the 6 wt.% sample since the quantity of catalyst was only 0.055 g. The 26-wt.%-loaded sample achieved 35% destruction at 150°C , which was significantly higher than the powder sample.

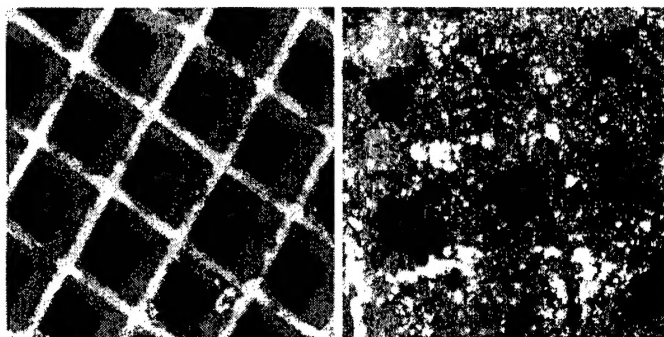


Figure 3. Magnified images (26x) of a 13-wt.% alumina coated monolith (left) and a 26-wt.% catalyst coated monolith (right).

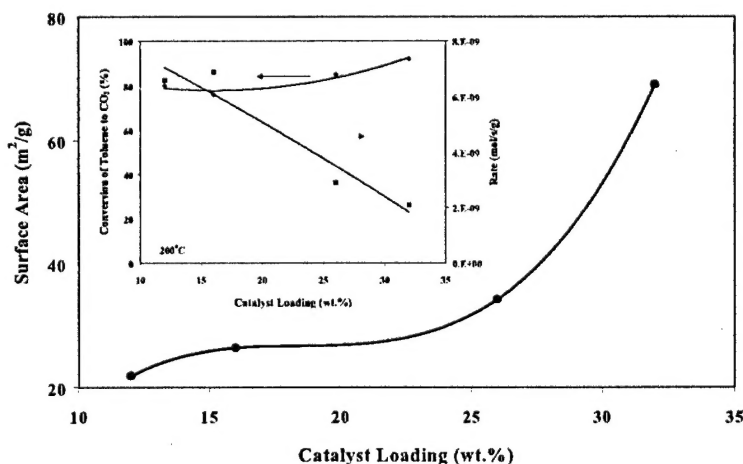


Figure 4. Plot showing the effect of catalyst loading on surface area, percent conversion of toluene to CO_2 , and rate of toluene destruction. The catalyst was MMO1. The toluene concentration was $\sim 100 \text{ ppmv}$ in air, and the W/F = 1.0 g/s/cm^3 . Conversion and rate measurements were obtained at 200°C .

B. Composition Optimization of Supported Mixed-Metal-Oxide Catalysts

Compositions of monolith-supported catalysts were experimentally optimized by varying the catalyst constituents and testing activity. An example of one such experiment is summarized in Figure 5 for destruction of toluene using a range of catalysts derived from MMO3. The catalyst is represented as $A_xB_{0.9-x}B'_{0.1}O_y$ and the abscissa of the plot indicates changes in the A/B ratio with B' held constant. At both 150° and 175°C, the maximum in the curve occurred at $x \approx 0.45$, which corresponded to a composition of $A_{0.45}B_{0.45}B'_{0.1}O_y$. Similar plots holding A constant and B constant generated equivalent results and indicated the above composition was optimal for toluene destruction with this category of catalysts.

Figure 6 shows the activity of $A_{0.45}B_{0.45}B'_{0.1}O_y$ as a function of temperature for three different W/F values. For each curve, essentially complete destruction of toluene was achieved by 190°C. However, the figure inset indicates that at 150°C, conversion of toluene to CO_2 decreased from 56% to less than 10% as W/F decreased from 1.4 to 0.28 g·s/cm³.

These optimization experiments were repeated for 22 different catalyst compositions, each containing up to four metal constituents. Activity was tested as a function of temperature using both toluene and 1-butanol. Results were input to a Multi-Simplex mathematical optimization procedure that suggests improved compositions based on the data. Preliminary compositions suggested by the procedure have been prepared and will be tested soon. Results from these tests also will be included in the Multi-Simplex procedure, and this process will be repeated until the optimum composition is identified.

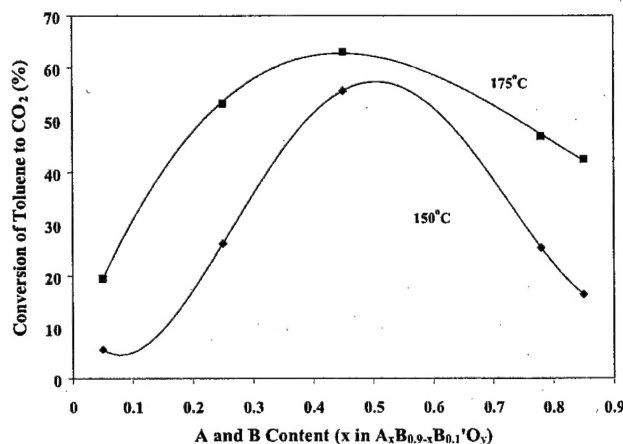


Figure 5. Plot showing conversion of toluene (100 ppmv in air) to CO_2 as a function of catalyst composition. $W/F = 1 \text{ g} \cdot \text{s}/\text{cm}^3$.

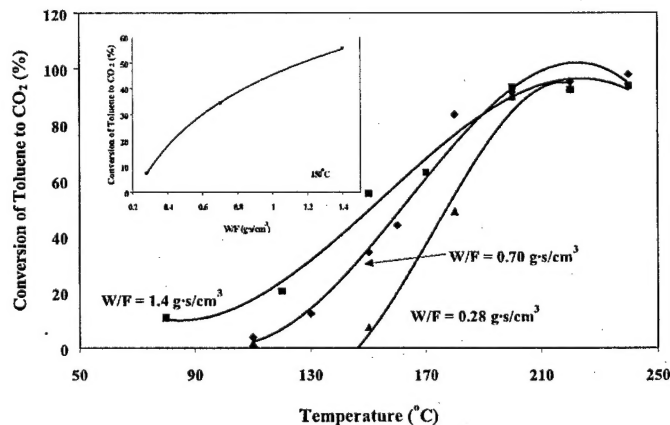


Figure 6. Plot showing activity of monolith-supported $A_{0.45}B_{0.45}B'_{0.1}O_y$ for conversion of toluene to CO_2 as a function of temperature and W/F. The inset shows activity versus W/F at 150°C.

C. Stability Testing

The most-active catalysts were tested for long-term stability in the presence of water vapor. Figure 7 summarizes the results for the catalyst indicated above as $A_{0.45}B_{0.45}B'_{0.1}O_y$ for destruction of MEK over a 1000-hour period. Moisture vapor was introduced by flowing the air line in Figure 1 through a heated water bubbler. This configuration enabled a moisture vapor content of ~ 45 mg/L to be maintained over the duration of the experiment. As shown in Figure 7,

there was a gradual increase in MEK destruction over the first 200 hours, air for the catalyst $A_{0.45}B_{0.45}B'_{0.1}O_y$. The MEK concentration was then complete destruction was ~ 100 ppmv and the water vapor content was ~ 45 mg/L. The gas flow rate and catalyst mass corresponded to $W/F = 0.5$ g/s/cm³.

Conversion of MEK to CO₂ dropped below 80% at 150°C, then below 40% at 100°C, and this level of conversion was maintained for 94 hours before terminating the test. The catalyst was heated in dry air at 250°C for over 300 hours to completely remove moisture, then tested for destruction of MEK at 150°C under dry conditions. In the absence of moisture, about 70% conversion of MEK to CO₂ was achieved at 150°C, which was slightly lower than with moisture. Equivalent results were obtained for other catalyst compositions using toluene and 1-butanol as the test VOCs, and generally, moist conditions improved VOC destruction by a few percent.

The catalyst $A_{0.45}B_{0.45}B'_{0.1}O_y$ also was tested for stability against sulfur and phosphorus poisoning. For these tests, conversion of thiophene (~ 410 ppmv in air) and dimethyl methyl phosphonate (DMMP, ~ 1250 ppmv in air) to CO₂ was measured at 250°C under dry conditions. As evident in Figure 8, results from these tests were much less encouraging than for moisture. Activity began to drop off immediately, and after only 100 hours on stream, conversion was less than 10%.

Conversion stabilized at about 5% for the remainder of test, which was 482 hours for thiophene. As anticipated, spectroscopic analysis

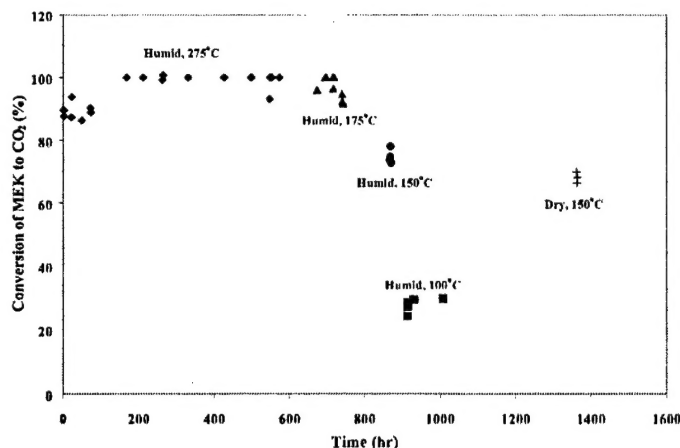


Figure 7. Plot showing conversion of MEK to CO₂ over time in moist air for the catalyst $A_{0.45}B_{0.45}B'_{0.1}O_y$. The MEK concentration was ~ 100 ppmv and the water vapor content was ~ 45 mg/L. The gas flow rate and catalyst mass corresponded to $W/F = 0.5$ g/s/cm³.

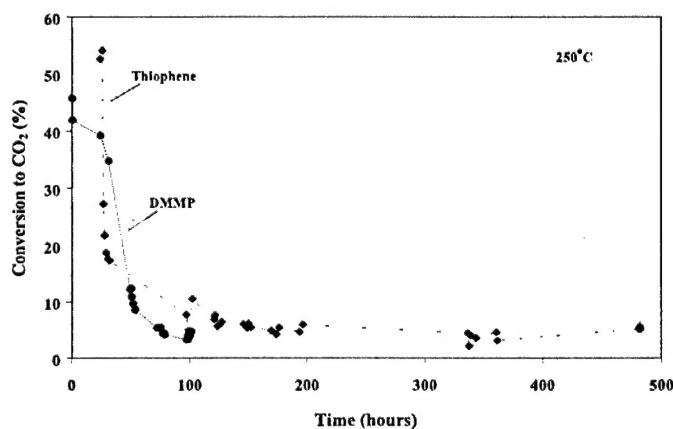


Figure 8. Plot showing conversion of thiophene (dotted line, 410 ppmv in air) and DMMP (solid line, 1250 ppmv in air) to CO₂ over time. The catalyst was $A_{0.45}B_{0.45}B'_{0.1}O_y$ and $W/F = 0.5$ g/s/cm³. The temperature was 250°C for the entire test.

(FTIR) of the catalysts indicated formation of sulfates and phosphates after the thiophene and DMMP tests, respectively. In fact, the thermodynamics of sulfate and phosphate formation for the constituents of this catalyst are very favorable, and modifications to this composition are necessary to target compounds containing these species.

CONCLUSIONS

Catalysts tested in this work demonstrated high activity for low-temperature destruction of the common VOCs toluene, 1-butanol, and MEK. Catalysts with the best overall performance were multi-component metal oxides selectively derived from single-component precursors. Under practical conditions, these catalysts (without precious metals) generated complete conversion of 1-butanol to CO₂ at 150°C, 69% conversion at 100°C, and 15% conversion at 80°C. For toluene, complete conversion at was achieved 200°C, and greater than 30% conversion at 150°C. These results demonstrated that substantial improvements in oxidation activity of metal-oxide-based materials can be achieved with relatively minor modifications in composition. Activity was retained when the catalysts were deposited onto cordierite monoliths, and the deposition method made it easy to achieve the target composition. Finally, monolith-supported catalysts were stable in moisture, but were quickly poisoned by sulfur and phosphorous compounds due to formation of sulfates and phosphates.

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KEY WORDS

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